

# **Thermal Expansion and Low Temperature Phase Transition in $K(x)Na(1-x)MgF_3$**

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**Introduction:** The perovskite structure is of the form  $ABX_3$ . It consists of corner-sharing B-X octahedra that house A cations in 12-fold coordination. Interest in this unique structure stems from a central role in Earth Science: Ferroelastic phase transitions in the perovskite  $MgSiO_3$  may explain observed seismic discontinuities in Earth's lower mantle [Shim and Jeanloz 2002]. Multiple industrial applications add interest to perovskite-structured materials, which have found applications ranging from substrates for superconductors [Kawasaki 1999] to electrolytes in solid state fuel cells [Ishihara 1996].

$K(x)Na(1-x)MgF_3$  end member,  $NaMgF_3$ , is orthorhombic and isostructural to  $MgSiO_3$  thus, may be used as a proxy for determining structural behavior at extreme conditions [O'Keeffe 1979]. Two previous studies involving substitution of K for Na in  $NaMgF_3$  has reported complete solubility. Phase transitions, first tetragonal ( $P4/mbm$ ) and then cubic ( $Pm-3m$ ) where  $x = \sim .35$  and  $x = \sim .40$  respectively, were also reported [Zhao 1998, Chakhmouradian et. al 2001]. These previous studies have disagreed upon the existence of two-phase regions delineating miscibility gaps within the solid solution. Also, neither study can justify the absence of long-range ordering of A cations at intermediate compositions.

**Methods and Materials:** The polycrystalline sample of  $K(x)Na(1-x)MgF_3$  was prepared in air using conventional solid state methods. High-resolution x-ray powder diffraction patterns were collected at a wavelength of 0.704702 angstrom using a position-sensitive detector with a spatial resolution of less than 50 microns. Samples were housed in 0.2 mm diameter quartz capillaries, mounted in a closed-cycle helium cryostat. Data were collected at temperatures increasing from 20 K in  $\sim 50$  K increments to 250 K on samples of various compositions;  $x = (0.0, .15, .30, .35, .40, .45, .50, .55, .60, .70, .80, .90, 1)$ .

**Results:** X-ray diffraction patterns were input into EXPGUI GSAS and calculated structural models were refined using Rietveld methods to extract precise values of unit cell volumes, atomic positions, K and Na occupancies, and phase fractions. The results of the refinement indicate the presence of two-phase regions within the solid solution at low temperatures. The unit cell volume of each composition was found to decrease uniformly. Thermal expansion of each composition will be calculated using methods described by Fei (1995).

The most striking structural change at low temperature is observed in a composition where  $x = .35$ , a mixture of about 10% orthorhombic ( $Pbnm$ ) and 90% tetragonal ( $P4/mbm$ ) phases at room temperature. An orthorhombic super-lattice triplet (marking anti-phase octahedral tilt) emerges at 20 K, redistributing the calculated proportion of each phase to 1:1. This reflection subsides between the measurements at 250 K and 300 K, but does not completely disappear in the room temperature data.

The results of this study suggest a structural model based on short-range octahedral distortion caused by anti-domain boundaries in orthorhombic (Na rich) and cubic (K rich) regions.

**Conclusions:** The low temperature phase redistribution observed where  $x = .35$  may also be pressure induced and will be the subject of further study within the diamond cell. This X-ray analysis will be included in a detailed high-resolution MAS NMR study, which hopes to illuminate the role of octahedral distortion and domain boundaries in this system

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## **References:**

- Chakhmouradian, A.R., Ross, K., Mitchell, R.H., and Swainson, I. (2001) "The crystal chemistry of synthetic potassium-bearing neighborite",  $(Na_{1-x}K_x)MgF_3$ . *Physics and Chemistry of Minerals*, 28(4), 277-284.
- Fei, Y. AGU Reference Shelf 2: Mineral Physics and Crystallography - A Handbook of Physical Constants, edited by T. J. Ahrens, pp. 29-44. Washington: AGU.
- Ishihara, T., Matsuda, H., binBustam, M.A., and Takita, Y. (1996) "Oxide ion conductivity in doped Ga based perovskite type oxide". *Solid State Ionics*, 86-8, 197-201.
- Kawasaki, M., Izumi, M., Konishi, Y., Manako, T., and Tokura, Y. (1999) "Perfect epitaxy of perovskite manganite for oxide spin- electronics". *Materials Science and Engineering B-Solid State Materials For Advanced Technology*, 63(1-2), 49-57.
- O'Keeffe, M., Hyde, B.G., and Bovin, J.O. (1979) "Contribution to the Crystal-Chemistry of Orthorhombic Perovskites -  $MgSiO_3$  and  $NaMgF_3$ ". *Physics and Chemistry of Minerals*, 4(4), 299-305.
- Shim, S.H., and Jeanloz, R. (2002) "P-V-T equation of state of  $MgSiO_3$  perovskite and the chemical composition of the lower mantle". *Geochimica Et Cosmochimica Acta*, 66(15A), A708-A708.
- Zhao, Y.S. (1998) "Crystal chemistry and phase transitions of perovskite in P-T-X space: Data for  $(K_xNa_{1-x})MgF_3$  perovskites". *Journal of Solid State Chemistry*, 141(1), 121-132.